

BIOSORPTION OF AQUEOUS METAL IONS AND METAL ION MIXTURES ONTO GROUND PEANUT HULLS

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

By

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“But my life is worth nothing to me unless I use it for finishing the work assigned me by the Lord Jesus - the task of testifying to the good news of God’s grace.” -Acts 20:24 NIV

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LIST OF ABBREVIATIONS

AMD	Acid mine drainage
b	Relative binding strength (ppm^{-1})
c	Concentration of standards used in determining LOD and LOQ (ppm)
C_e	Equilibrium concentration (ppm)
C_f	Final metal concentration after mixing with hulls (ppm)
C_i	Initial metal concentration before mixing with hulls (ppm)
Cd	Cadmium
CFSE	Crystal field stabilization energy
Cu	Copper
FAAS	Flame atomic absorption spectroscopy
LOD	Limit of detection (ppm)
LOD'	Limit of detection for one standard (ppm)
LOQ	Limit of quantitation (ppm)
LOQ'	Limit of quantitation for one standard (ppm)
μ	Mean atomic absorption signal for determining LOD and LOQ
M	Metal ion
M	Molar mass
m	Mass of hulls (g)
q_e	Surface coverage ($\text{mg M}^{2+}/\text{g hull}$)
Q_o	Adsorption capacity ($\text{mg M}^{2+}/\text{g hull}$)
R	Ideal gas constant
r	Radius of hull particle
SAVR	Surface area volume ratio (μm^{-1})
σ	Standard deviation of atomic absorption signals for determining LOD and LOQ
T	Temperature
V	Volume of solution (mL)
v_{rms}	Root mean square velocity

ABSTRACT

BIOSORPTION OF AQUEOUS METAL IONS AND METAL ION MIXTURES ONTO GROUND PEANUT HULLS

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The purpose of this research project was to investigate the adsorption of heavy metals onto unmodified and modified ground peanut hulls to determine their compatibility as a biosorbent for heavy metal containing aqueous environments. The adsorptions of copper and cadmium were assessed individually, and in combination, through a series of batch studies to investigate the metal specific adsorption capacities and competition between metal ions for binding sites using unmodified and modified 125-250 μm , 250-500 μm , and 500-1000 μm hulls. The results from unmodified and modified hulls were compared to determine that modified hulls have higher adsorption capacities for copper and cadmium than unmodified hulls of similar size due to increased porosity following the bleaching process. In single metal solutions, there was not a significant difference in the adsorption capacities for copper and cadmium. However, hulls have higher adsorption capacities for copper than cadmium in binary metal solutions, which may be attributed to kinetics. The factors that influence the adsorption of copper and cadmium onto ground peanut hulls are the nature of the ion, including polarizing power and ionic radius, and the material used as the sorbent, with the type of material playing the largest role in determining the adsorption of metals.

CHAPTER ONE: INTRODUCTION

Motivation

Large industries such as mining and coal fueled power plants produce heavy metal containing waste. However, unlike other wastes, heavy metal containing wastes are not biodegradable, and therefore, can accumulate in ground water or rivers when not managed properly, forever damaging the surrounding ecosystems and wildlife. Additionally, heavy metals that reach natural water sources are likely to accumulate in the food chain and cause serious illness in humans if enough of the material accumulates in the body.^{1,2} It is therefore necessary to remove heavy metals from waste waters to prevent their release into the environment.³

Some conventional methods for heavy metal removal from waste water include chemical precipitation, ion exchange, reverse osmosis, membrane electrolysis, and coagulation-flocculation. However, these practices can be costly and have drawbacks such as toxic sludge generation, high chemical and energy consumption, metallic hydroxides production, scaling of CaCO_3 and CaSO_4 , and the need for trained personnel and additional pretreatment procedures.¹ Due to the many disadvantages of conventional methods, researchers continue to investigate and develop safe and cost effective ways of removing heavy metals from these wastes.

Background

Adsorption is a method in which a substance (the adsorbate) is removed from an aqueous state by becoming trapped on the surface of a solid (the adsorbent) through physical or chemical interactions.⁴ Similarly, biosorption is the removal of metal or metalloid species, compounds, and particulates from solution using a biological material (the biosorbent).⁵ For waste water remediation, this process is advantageous because it allows aqueous heavy metals to be extracted from solution without the addition of other harmful chemicals. This process is highly dependent upon the solid's surface area and reactivity, so in many cases the adsorbent must first be chemically treated in order to maximize these properties. Many of these treatment techniques include dying

or rinsing the substance in an acid or base to remove soluble components of the material that may interfere with its adsorption capacity, increase pore size, or to produce charged attachment sites on the surface to which metal ions can bind.^{2,4}

In a study of over 100 research articles, Kurniawan et al. evaluated many low-cost agricultural wastes to determine their efficiency as biosorbents.⁴ Many different agricultural substances are effective as biosorbents, including hazelnut shells, orange peels, and soybean hulls.⁴ Agricultural products containing significant amounts of lignin and cellulose (lignocellulosic materials) are highly capable of extracting heavy metals because they contain functional groups necessary to bind heavy metals, such as hydroxyl groups, and carbonyls.^{4,6} A study conducted by Johnson et al. used peanut hulls, containing 34-45% cellulose and 27-33% lignin and with a porosity of 61.70%, for the adsorption of Cu(II) from waste water with a success rate of 92% within the first 50 minutes.³

Several additional adsorption studies revealed that pretreating a biosorptive material can drastically increase the adsorption of the material.^{4,5} One study used jute fibers to adsorb copper.⁶ The oxidation of the jute fibers caused an increase in adsorption capacity from 4.23 mg Cu/g fiber to 7.73 mg Cu/g fiber.⁶ Additionally, a study using formaldehyde treated sawdust showed a cadmium adsorption of 9.29 mg Cd/g sawdust.² One pretreatment of lignocellulosic biosorption material that has been shown to increase binding sites used for metal adsorption is bleaching.⁶ Previous studies have shown that the bleaching of peanut hulls involves the removal of lignin and other alkaline soluble components of the hulls, increasing the porosity and surface area of the hulls.⁷ This increased surface area allows for more accessibility of binding sites within the hulls, increasing the likelihood of heavy metal ions to bind to the surface of the hulls. Additionally, the bleaching process maximizes the material's adsorptive capabilities by oxidizing hydroxyl groups on the hull surface to carboxylate groups, thereby increasing the number of heavy metal binding sites.⁶

The adsorption of multimetal mixtures has also been investigated to evaluate the competi-

tion for sorption sites among metals in solution. Multi-metal mixtures more closely resemble real waste water effluent in which multiple metals may be found within the same aqueous environment. For example, abandoned and neglected mines often result in heavy metal containing runoff and acid mine drainage (AMD), which drains into nearby groundwater and streams.^{8,9}

An adsorbent that has been used for the investigation of multimetal adsorption is kaolinite. Kaolinite is a silicate complex commonly found in tropical soils that consists of a 1:1 aluminum-silicon sheet ratio bound together through the sharing of oxygen atoms and has a small overall negative charge.¹⁰ Through experimentation using kaolinite, copper was observed to have a higher adsorption capacity (Q_o) than cadmium in single and multi-metal mixtures.¹⁰ These results were attributed to copper being able to hydrolyze more readily, causing it to be more likely to interact with the materials hydroxylated surface.¹⁰ Another study observed similar results of copper and cadmium binding in decreasing adsorption capacity using carbon nanotubes as the adsorbent.¹¹

Adsorption capacities for biosorption studies are commonly calculated using the Langmuir model, as shown in Equation 4, due to the model's ability to predict a wide range of experimental data.⁷ The Langmuir model is a mono-layer adsorption isotherm that uses two fitting parameters, relative binding strength (b) and adsorption capacity (Q_o), along with the assumptions that the sorbent surface is homogenous with all surface binding sites are equivalent, and that there are no surface interactions between adjacent sorbate molecules.^{12,13}

Research Goals

The purpose of this research project was to investigate the adsorption of heavy metals onto modified and unmodified ground peanut hulls to determine their compatibility as a biosorbent for heavy metal containing aqueous environments. In this project the use of modified, also known as bleached, peanut hulls for the adsorption of heavy metals was investigated and compared to the use of unmodified hulls. More specifically, the adsorption capacity and binding strength of copper and cadmium onto modified and unmodified hulls was evaluated, and the degree to which

the metals compete with one another for adsorption sites was determined. Adsorption studies assessed the individual adsorption behavior of copper and cadmium onto ground peanut hulls with size ranges of 125-250 μm , 250-500 μm , and 500-1000 μm , as well as the adsorption of these metals to unmodified and modified hulls when they were part of a binary mixture.

CHAPTER TWO: EXPERIMENTAL

Materials

The peanut hulls used for the procedure were collected from Laura Lynn brand roasted in the shell peanuts purchased from Ingles, Sylva, NC. Sodium hydroxide pellets (reagent grade) were purchased from S & S Scientific Supply. Cupric dihydrate chloride ($\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, laboratory grade), cadmium chloride ($\text{CdCl}_2 \cdot \frac{3}{2} \text{H}_2\text{O}$, certified ACS), nitric acid (certified ACS plus), Hydriion pH 4 buffer capsules containing potassium bipthalate, and 30-35 % hydrogen peroxide were purchase from Fisher Scientific. All materials were used without further purification or modification unless otherwise noted. All water used in the study was ultrapure water with $18.2 \text{ cm } \Omega$ from a Barnstead water filtration system (Thermo Scientific, Model 7119).

Hull Preparation

The hulls were manually separated from the seed coats and peanuts. The peanut hulls were ground using a Hamilton Beach Fresh Grind Coffee Grinder (#80335) and separated by size using U.S.A. Standard Test Sieves (ASTM E-11 Specification, Fisher Scientific Co.) with mesh sizes 1 mm, 500 μm , 250 μm , and 125 μm on a sieve shaker (Model SS-15, Gilson, Inc.). The collected hulls were washed with 60 °C H_2O , followed by ice cold H_2O , and then dried at 50 °C in an air oven (VWR International, Model 1300U). Hulls retained by the 500 μm , 250 μm , and 125 μm sieves were used for metal adsorption studies. Hulls retained by the 125 μm sieve were 125-250 μm in their widest dimension. Hulls retained by the 250 μm sieve were 250-500 μm in their widest dimension. Hulls retained by the 500 μm sieve were 500-1000 μm in their widest dimension.

Separation

About 20 g of dry, washed hulls were added to water while stirring. After 2-5 minutes, the hulls separated into two layers; one layer floated on the surface of the water, and one layer sank to the bottom of the vessel. The floating, low density hulls were decanted into a second beaker, stirred,

and allowed to separate again. The decantation was repeated once more. The floating, low density hulls and the bottom layer, high density hulls, were filtered separately and dried at 50 °C in an air oven. This procedure was repeated once more to ensure total separation of the high and low density hulls. However, for the majority of the experiments described here, this separation was not performed, and a natural mixture of high and low density hulls were used.

Modification

Modification of the ground peanut hulls was performed using a method of bleaching developed by Shukla⁶ and further modified for peanut hulls by Davis.¹⁴ A 1 L water-jacketed beaker equipped with a stir bar on a stir plate was connected to a refrigerated bath (Fisher Scientific Isotemp, model number 4100R20) set to 20 °C. Thermometer and pH probes (Vernier) were used to monitor temperature and pH throughout the bleaching reaction. About 13 g of sodium hydroxide pellets were added to 50 mL of H₂O in the water-jacketed beaker and stirred until dissolved. Cold 35 % hydrogen peroxide (300 mL) was added to the mixture resulting in a 0.97 M sodium hydroxide solution and 35 % hydrogen peroxide mixture. The solution stirred until a constant temperature of 20 °C was reached. Approximately 7 g of hulls were added to the solution, and a nylon netting was secured over the opening of the beaker to contain the hulls within the beaker if the foam produced from the reaction overflowed. The temperature bath was turned off after two hours and the reaction was left to continue stirring for four hours. The hulls were then filtered and rinsed with cold H₂O until the rinse water pH was neutral. The hulls were then dried at 50 °C in an air oven.

Limit of Detection and Limit of Quantitation

Determination of metal concentrations was carried out using a Perkin Elmer flame atomic absorption spectrometer (FAAS, PinAAcle900F). Three replicate absorption measurements were collected for each sample at a flow rate of 2.5 L/min and the mean was used to calculate the concentration. The limit of detection (LOD), the lowest concentration detectable by the instrument, was calculated for copper and cadmium individually by following the FAAS guide provided by Perkin

Elmer.¹⁵ Two standards were prepared separately for FAAS analysis. The first standard was prepared with a concentration five times the expected detection limit, while the second standard was prepared to be twice the concentration of the first standard. The expected detection limit was determined by looking at previously collected data from standards used for analysis. For copper, standard concentrations of 0.2917 ppm and 0.5889 ppm were selected. For cadmium, the standard concentrations were 0.0558 ppm and 0.1067 ppm. 5% HNO₃ was used in the preparation of the standards and was used as a blank between measurements.

Once optimal flame conditions were established, the standards were analyzed in the following pattern: blank, low concentration standard, blank, high concentration standard, blank, low concentration standard, etc. until 10 readings of each standard had been performed.

The blank signals before and after each standard measurement were averaged, and the average value was subtracted from each standard's signal. The 10 corrected signals calculated for each standard were then averaged (μ) and the standard deviation (σ) was calculated. The limit of detection for an individual standard (LOD') can be calculated where c is the known concentration of the standard:¹⁵

$$LOD' = \frac{3\sigma c}{\mu} \quad (1)$$

Once the LOD' was calculated for each standard, the two values were averaged, resulting in the reported limit of detection (LOD).

The limit of quantitation (LOQ) is the lowest concentration quantifiable by the instrument. This value is used to determine the lowest possible concentration that can be confidently analyzed. The LOQ' for each of the 2 standards was calculated using Equation 2, and then averaged to find the reported LOQ.¹⁵

$$LOQ' = \frac{10\sigma c}{\mu} \quad (2)$$

Adsorption Studies

Single Metal Adsorption Studies

The adsorption capacity for each hull type was assessed through batch studies of individual metal ions using modified and unmodified hulls. The metal ions investigated were Cu^{2+} and Cd^{2+} . Adsorption studies were conducted using a series of 12 solutions ranging in metal ion concentration between 10 ppm and 2000 ppm. A stock solution with a metal concentration of 2000 ppm was prepared using either $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ or $\text{CdCl}_2 \cdot \frac{3}{2} \text{H}_2\text{O}$ and pH 4 buffer capsules, then used to prepare 11 additional solutions through serial dilution.

In each adsorption study, 2 g of hulls were mixed with the 12 prepared solutions for 24 hours on a tube revolver (Scientific Tube Revolver, model #88881001) at a revolution rate of 40 rpm. After mixing, the hulls from each solution were filtered using hydrophilic $0.45 \mu\text{m}$ nylon syringe filters attached to 10 mL syringes. The solutions were then diluted to within the linear range for the metal ion absorption reported in the FAAS guide¹⁵ for copper and cadmium.

The solutions were analyzed using the flame atomic absorption spectrometer using the same parameters that were used for LOD and LOQ determination. The metal ion concentrations of the diluted solutions were determined using a calibration curve from standards in the concentration range of 0.5-12 ppm, which is above the limit of quantitation.

Figure 1 shows a schematic diagram of the adsorption of metal ion, M, to peanut hulls. In this figure, C_i represents the initial metal ion concentration before hulls were added, and C_f represents the final metal ion concentration after the hulls have been mixed with and filtered out of the solution. After the hulls were filtered out of solution, the remaining solution was analyzed with FAAS to determine C_f .

The concentrations of metal ions before and after mixing with the hulls were used to quantify the surface coverage of the metal ion (q_e , mg M/g hull) using Equation 3,

$$q_e = \frac{(C_i - C_f)V}{m} \quad (3)$$

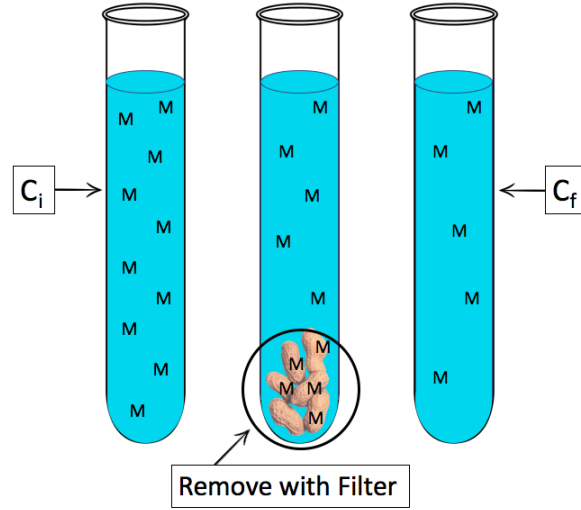


Figure 1. A schematic representation of the metal ion adsorption process.

where V is the volume of solution and m is the mass of hulls mixed with the solution. The surface coverage (q_e) was plotted as a function of the equilibrium concentration, C_e ($C_e = C_f$). The data was then fit to the Langmuir equation

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (4)$$

where Q_o is the adsorption capacity of the hulls and b is the relative binding strength. These parameters were extracted from the fit using LoggerPro software (Vernier). The root mean square error (RMSE) of the adsorption capacities for single metal adsorption studies were between 0.1 and 1.7.

Binary Metal Adsorption Studies

The competition between metals for hull binding sites in solution was assessed through batch studies of binary metal ion mixtures using modified and unmodified hulls. The procedure was the same as for single metal adsorption studies except the solutions were prepared using equal concentrations between 0 ppm and 2000 ppm of each metal (0-4000 ppm total metal ion concentration). The solutions were diluted to within the linear range of 1-2 ppm for cadmium¹⁵ be-

fore being analyzed using FAAS. Standards were prepared similarly to those used in single metal studies, and contained a concentration of 0.5-12 ppm of copper and cadmium each to mimic the matrix of samples.

The concentrations of individual metal ions before and after mixing with the hulls were used to quantify the surface coverage of the metal ions (q_e), and q_e vs. C_e was fit to the Langmuir isotherm (Equation 4) to determine Q_o and b in the same manner as for the single metal adsorption studies. The RMSE values for binary metal mixture adsorption capacities were between 0.2 and 1.2.

CHAPTER THREE: RESULTS AND DISCUSSION

Hull Separation

Figure 2 shows the first separation of 500-1000 μm hulls. High density hulls are darker in color, and appear more coarse in texture, while low density hulls are lighter in color, and appear thinner, more flaky, and also contain long, slender fibers, as shown in Figure 3

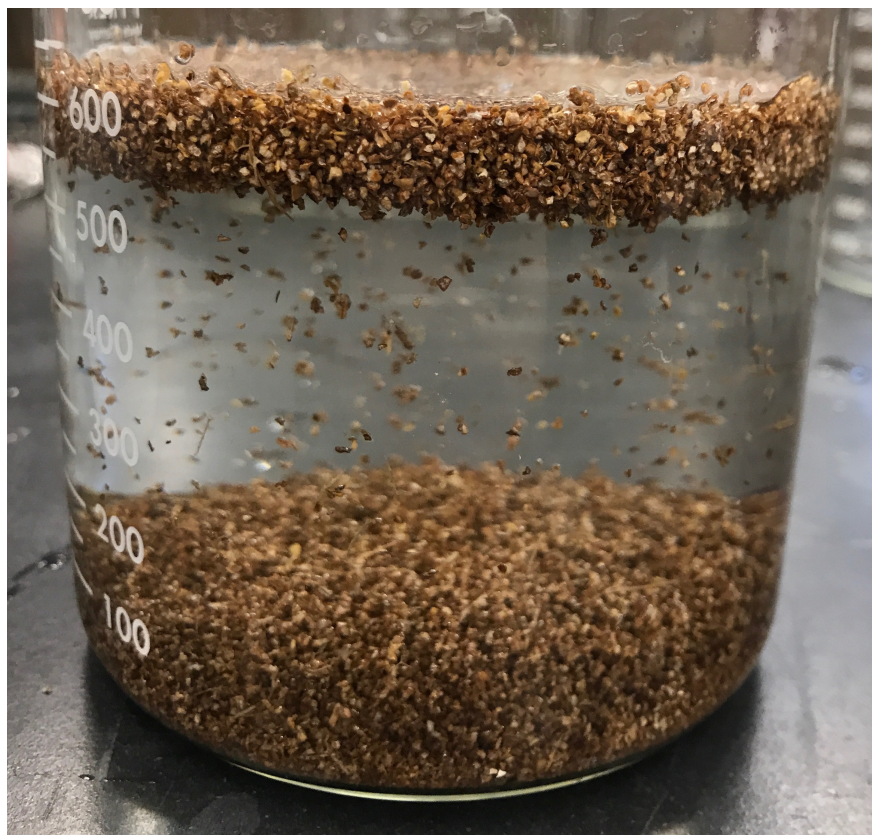


Figure 2. Separation of 500-1000 μm hulls.

Figure 4 shows the adsorption isotherms fit to the Langmuir equation (Equation 4) for two trials of cadmium adsorption onto unmodified high density, 500-1000 μm hulls. Adsorption isotherms were not reproducible from trial to trial. A similar variation from trial to trial was also observed for the adsorption of copper and cadmium to unmodified, low density hulls and modified, high

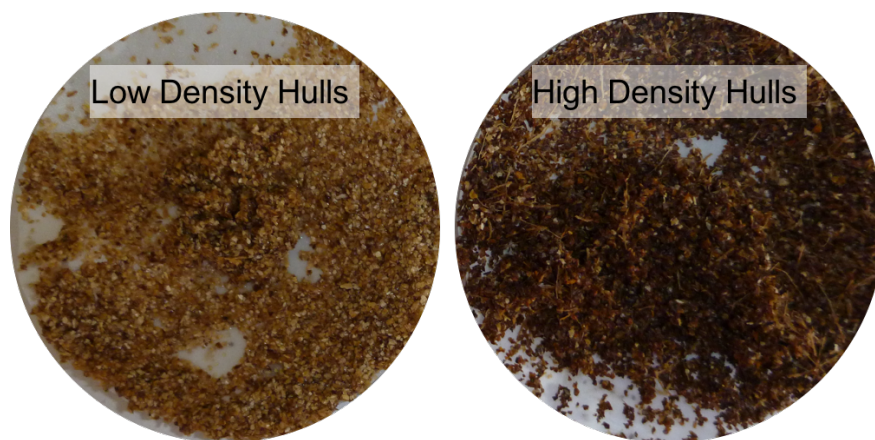


Figure 3. Separated high and low density 500-1000 μm hulls.

and low density hulls (not shown). The lack of reproducibility could be due to hull sample variation from trial to trial. It is possible that even after 2 separations there were high density hulls trapped in the low density layer or vice versa, which would result in heterogeneity from sample to sample and cause irreproducible results from trial to trial. Isotherm reproducibility was improved when unseparated hulls were used, so a natural mixture of high and low density hulls was used for the remainder of the experiments.

Hull Modification

The ground peanut hulls are lighter in color after being mixed with the alkaline peroxide solution. The reaction produces foam throughout the reaction. Approximately 1 hour into the reaction, the foam layer rises quickly, reaching a maximum height of approximately three inches in the 1 L reaction vessel before subsiding. This coincides with the pH and temperature increase shown in Figure 5 for the bleaching of 250-500 μm hulls. Similar temperature and pH profiles are observed for all bleaching experiments. During the bleaching of 125-250 μm hulls, the foam layer rises more quickly, reaching the brim of the reaction vessel within the first 2 hours, and during the bleaching of 500-1000 μm hulls, the foam layer rises more slowly, reaching the brim of the reaction vessel between 2 and 3 hours. In all cases the pH increase and temperature spike occurred between 2 and 4 hours, indicating that the reaction is completed in that timeframe. The tempera-

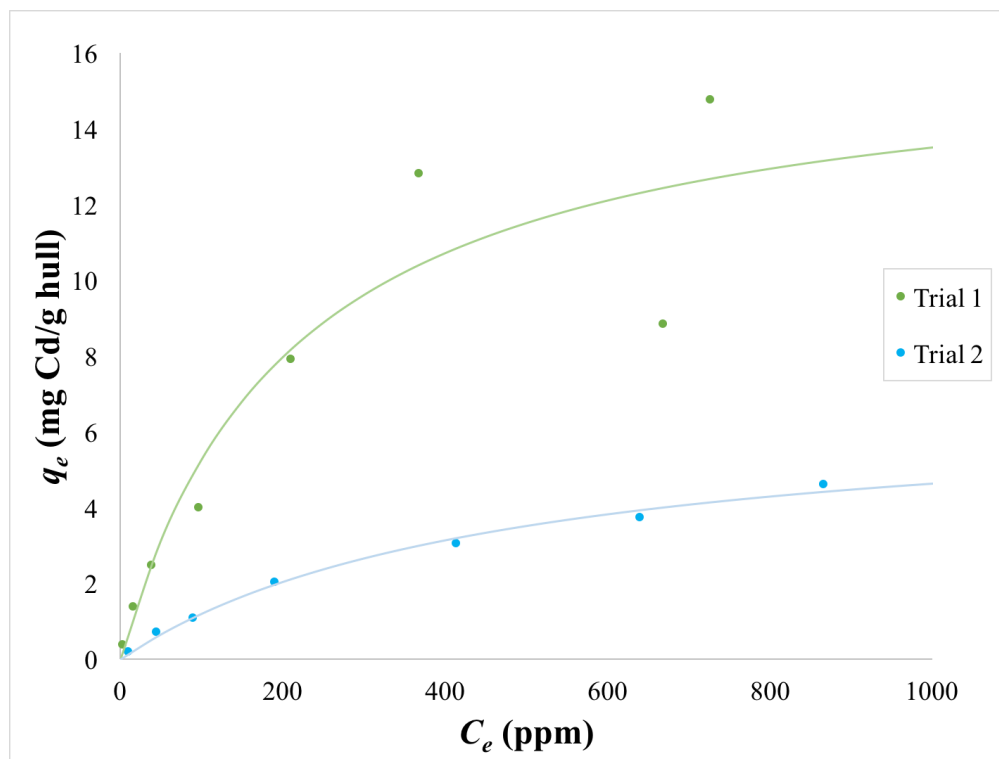


Figure 4. Adsorption isotherms for cadmium adsorbed onto unmodified, high density 500-1000 μm hulls. The graph represents the data collected from 2 trials. Solid lines are the fits to the Langmuir equation.

ture increase is a result of the reaction being exothermic, while the increase in pH is presumably due to the alkaline nature of species being extracted from the hulls, such as lignin.⁷

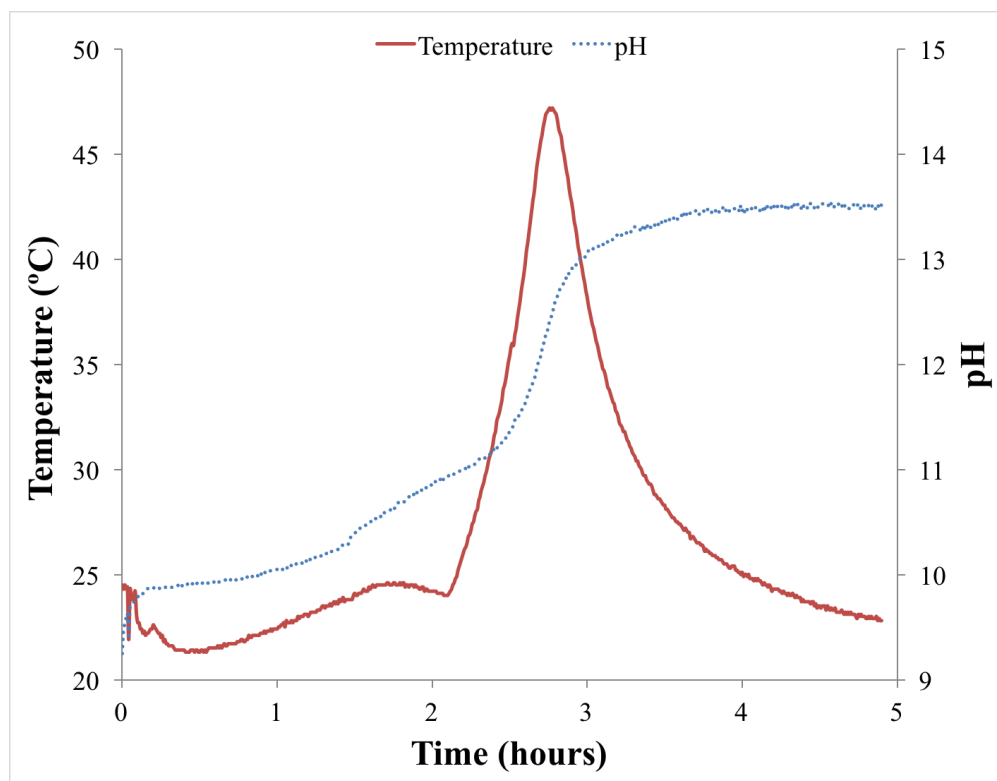


Figure 5. The pH and temperature recorded during the modification of 250-500 μm hulls.

Figure 6 shows the physical characteristics of unmodified and modified ground peanut hulls. The hulls have a tendency to aggregate when dried. The degree of aggregation increases as hull size decreases. Some aggregates fell apart when added to metal ion solutions; however, some of the aggregates remain bound in solution after mixing. This could negatively impact adsorption by decreasing surface area and Q_o . Aggregates could be broken apart by crushing with a mortar and pestle, but that could also alter the individual hull particle size and was avoided. As shown in Figure 6, the 500-1000 μm unmodified hulls have a variety of colored, shaped, and textured pieces within the sample. This could be attributed to the hulls having greater heterogeneity. Larger particles will have greater variation in both physical and chemical composition than smaller particles.

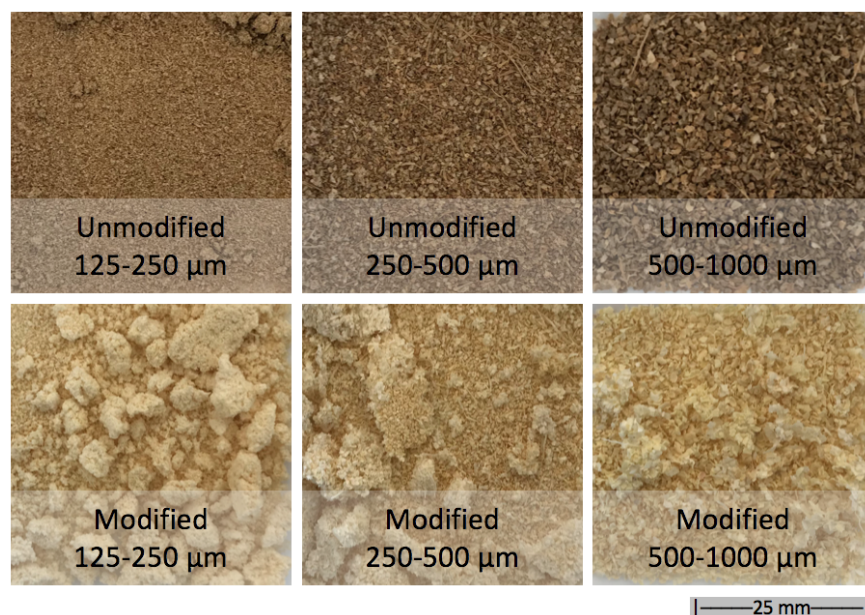


Figure 6. Unmodified and modified ground peanut hulls.

Limit of Detection and Limit of Quantitation

Table 1 shows the values used for the calculation of the LOD and LOQ. Reported uncertainties are the standard deviations. For copper, the LOD was determined to be $0.034 \text{ ppm} \pm 0.003 \text{ ppm}$ and the LOQ was determined to be $0.112 \text{ ppm} \pm 0.009 \text{ ppm}$. For cadmium, the LOD was determined to be $0.013 \text{ ppm} \pm 0.005 \text{ ppm}$ and the LOQ was determined to be $0.04 \text{ ppm} \pm 0.02 \text{ ppm}$. The calculated LOD and LOQ values indicated the minimum concentrations that can be reliably measured using FAAS. In all adsorption experiments described in the next section, the measurements were valid because all sample concentrations were above the LOQ.

Adsorption Studies

Single Metal Adsorption

Figure 7 shows adsorption isotherms for the adsorption of cadmium onto 125-250 μm , 250-500 μm , and 500-1000 μm unmodified hulls. For all hull size ranges, surface coverage (q_e) increases with increasing equilibrium concentration (C_e) for C_e less than 1000 ppm. However, the surface coverage at concentrations above 1000 ppm no longer follows the Langmuir model. Instead, q_e either

Table 1. Values used for the calculation of the LOD and LOQ of copper and cadmium.

	Copper		Cadmium	
	Standard 1	Standard 2	Standard 1	Standard 2
c (ppm)	0.2917	0.5889	0.0558	0.1067
σ (ppm)	0.0005	0.0006	0.0006	0.0003
μ (ppm)	0.01	0.03	0.006	0.01
Avg. LOD (ppm)	0.033 \pm 0.003		0.013 \pm 0.005	
Avg. LOQ (ppm)	0.112 \pm 0.009		0.04 \pm 0.02	

decreases or is far from the fit to the Langmuir equation. This non-ideal behavior could be caused by changes in metal speciation at higher concentrations. If present, these metal ion complexes could either bind differently to binding sites than low concentration species or remain in solution after dilution as a stable complex with a different absorption wavelength than the low concentration species, skewing the solution concentration measured by FAAS. Traditionally, adsorption concentrations have been reported out to 600 ppm or less.^{3,6,11} However, fitting the isotherm to too low of a concentration range could result in a large uncertainty in Q_o if the isotherm has not reached a maximum surface coverage. To compromise, isotherm data in single metal adsorption studies were reported from 0-1000 ppm.

Figures 8 through 11 show q_e vs. C_e data fit to the Langmuir equation (Equation 4) for the adsorption of copper and cadmium onto unmodified and modified hulls. From the fitting parameters, adsorption capacity (Q_o) and relative binding strength (b) were determined, and are summarized in Table 2, and Figures 12 and 13, respectively.

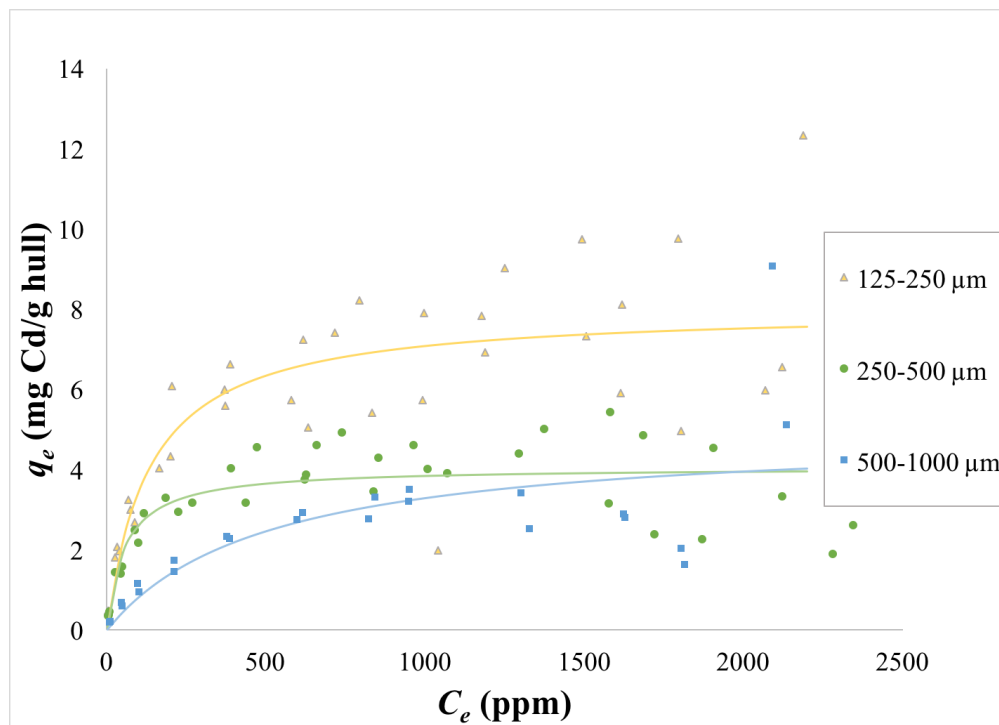


Figure 7. Isotherms of cadmium adsorbed to unmodified hulls in the 0-2000 ppm concentration range. Three trials of data are shown for 125-250 μm and 250-500 μm hulls, while two trials of data are shown for 500-1000 μm hull. Solid lines are the fits of the data to the Langmuir equation.

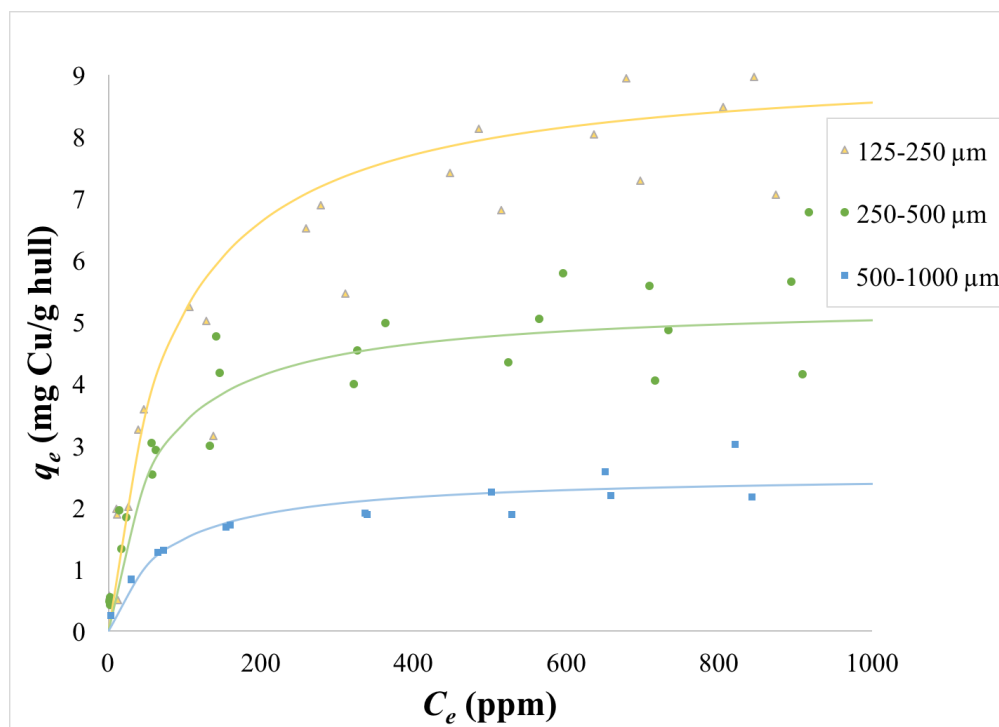


Figure 8. Isotherms of copper adsorbed to 125-250 μm , 250-500 μm , and 500-1000 μm unmodified hulls. The data shown for 125-250 μm and 250-500 μm hulls is from three trials. The data shown for 500-1000 μm hulls is from two trials. The solid lines are the fits to the Langmuir equation.

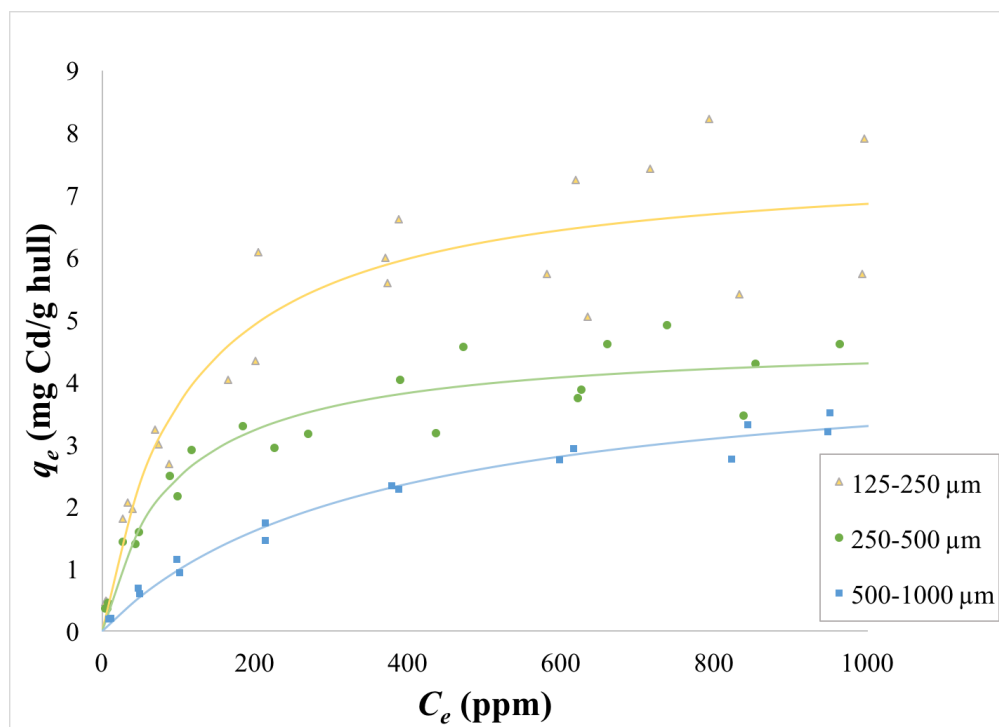


Figure 9. Isotherms of cadmium adsorbed to 125-250 μm , 250-500 μm , and 500-1000 μm unmodified hulls. The data shown for 125-250 μm and 250-500 μm hulls is from three trials. The data shown for 500-1000 μm hulls is from two trials. The solid lines are the fits to the Langmuir equation.

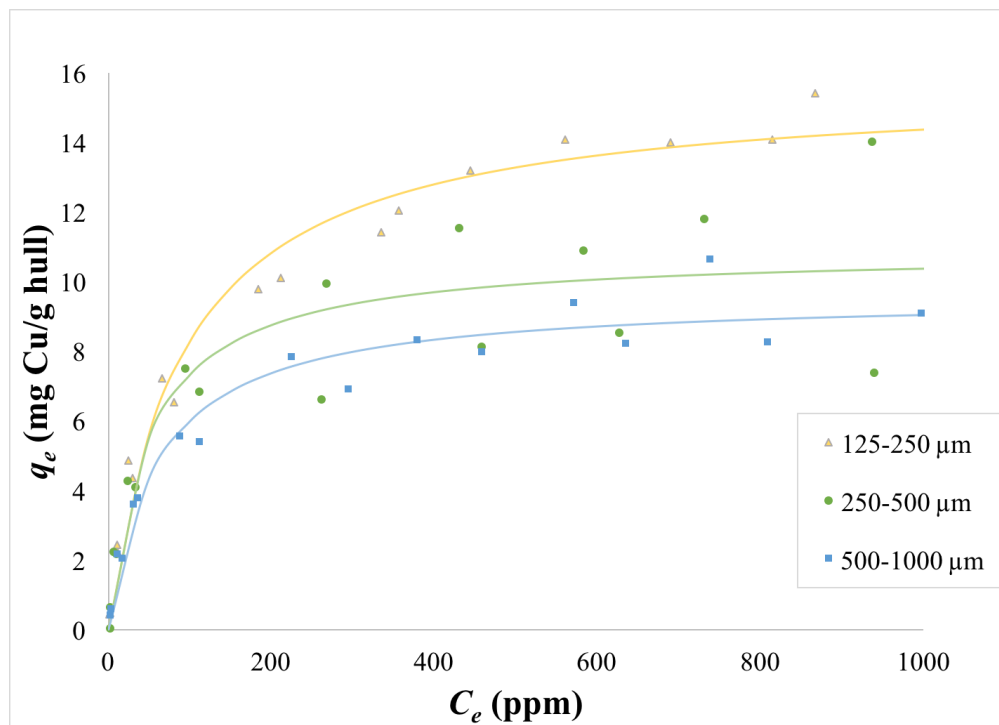


Figure 10. Isotherms of copper adsorbed to 125-250 μm , 250-500 μm , and 500-1000 μm modified hulls. The data shown for 125-250 μm and 250-500 μm hulls is from three trials. The data shown for 500-1000 μm hulls is from two trials. The solid lines are the fits to the Langmuir equation.

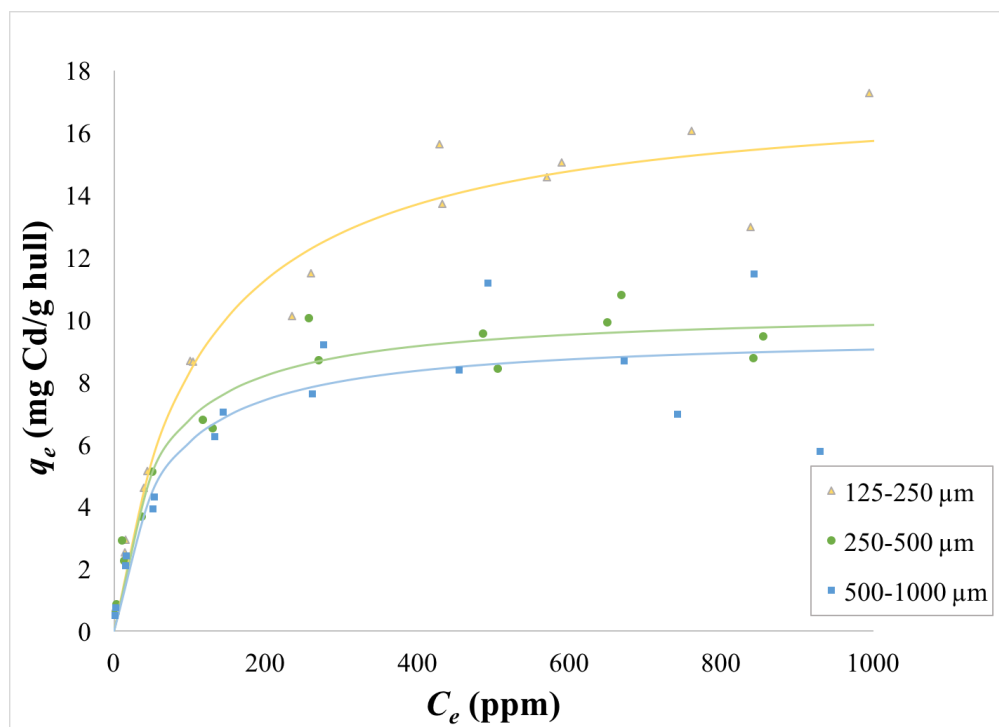


Figure 11. Isotherms of cadmium adsorbed to 125-250 μm , 250-500 μm , and 500-1000 μm modified hulls. The data shown for 125-250 μm and 250-500 μm hulls is from three trials. The data shown for 500-1000 μm hulls is from two trials. The solid lines are the fits to the Langmuir equation.

Table 2. Single metal adsorption capacities, Q_o (mg M/g hull), relative binding strengths, b (ppm^{-1}), associated uncertainties for unmodified and modified hulls. The data reported for unmodified 250-500 μm unmodified and modified hulls excludes one outlier data point.

Hull Type	Hull Size	Copper		Cadmium	
		Q_o	b	Q_o	b
Unmodified	125-250 μm	9 ± 2	0.011 ± 0.002	8 ± 1	0.009 ± 0.002
	250-500 μm	5 ± 1	0.020 ± 0.005	4.7 ± 0.7	0.011 ± 0.002
	500-1000 μm	2.5 ± 0.5	0.014 ± 0.004	4.4 ± 0.4	0.0028 ± 0.0004
Modified	125-250 μm	16 ± 2	0.011 ± 0.002	17 ± 2	0.009 ± 0.002
	250-500 μm	11 ± 4	0.021 ± 0.008	10 ± 2	0.019 ± 0.004
	500-1000 μm	10 ± 1	0.017 ± 0.003	10 ± 3	0.017 ± 0.007

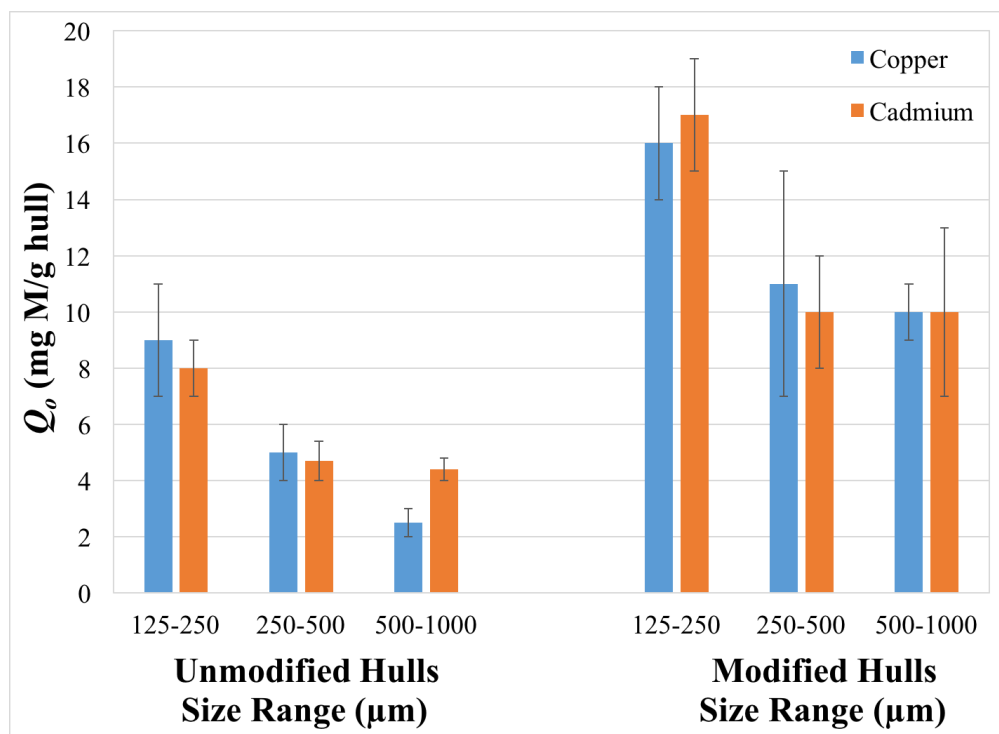


Figure 12. Adsorption capacities, Q_o (mg M/g hull), for copper and cadmium adsorbed onto 125-250 μm , 250-500 μm , and 500-1000 μm unmodified and modified hulls in single metal adsorption studies with their associated uncertainties, determined from the fits of the adsorption data to the Langmuir equation.

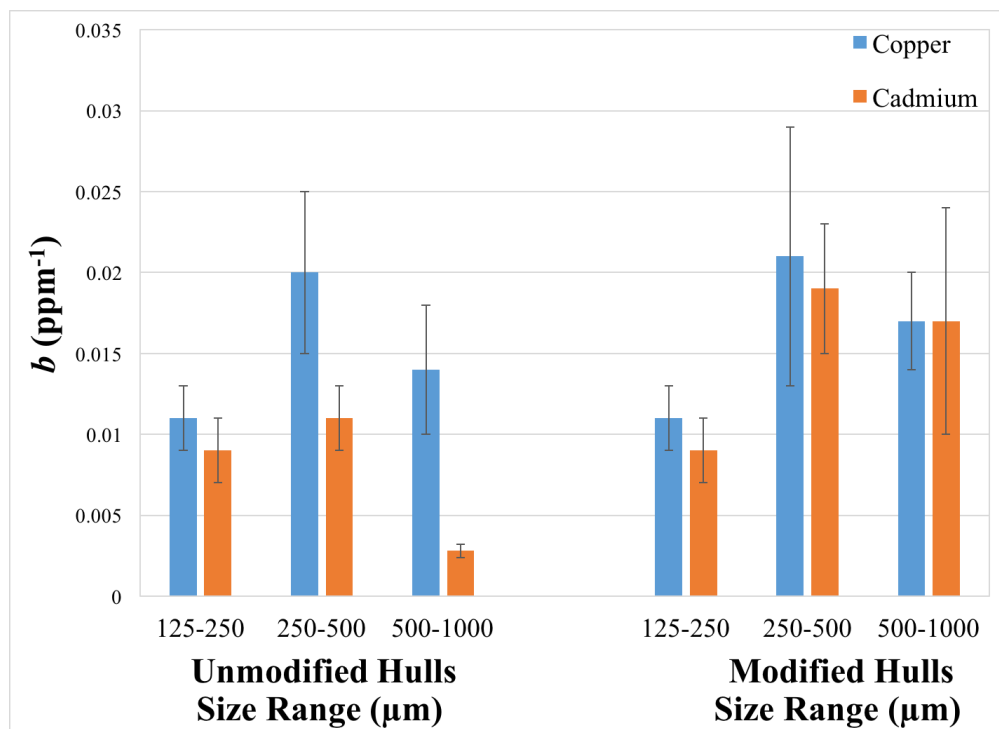


Figure 13. Relative binding strengths, b (ppm⁻¹), for copper and cadmium adsorbed onto 125-250 μm, 250-500 μm, and 500-1000 μm unmodified and modified hulls in single metal adsorption studies with their associated uncertainties, determined from the fits of the adsorption data to the Langmuir equation.

Effects of Hull Size. In all cases, 125-250 μm hulls showed a greater adsorption capacity for metals than 500-1000 μm hulls, indicating that as hull size decreases, Q_o increases. This increase is due to the increased surface area to volume ratio (SAVR), which provides a greater number of binding sites, thereby increasing Q_o . The surface area to volume ratio (SAVR) is the surface area per unit volume of hull, assuming a solid spherical particle, and was determined by dividing the surface area ($4\pi r^2$) by the volume ($\frac{4}{3}\pi r^3$). These values were calculated using Equation 5, where r is half the average particle diameter. The SAVR for each hull type are reported in Table 3 with the adsorption capacities and associated uncertainties for copper and cadmium. SAVR was approximated by assuming spherical particles with an average diameter at the midpoint of the size range. The correlation between Q_o and SAVR is shown in Table 3 and Figure 14.

$$\text{SAVR} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} \quad (5)$$

Table 3. Adsorption capacities, Q_o (mg M/g hull), for copper and cadmium adsorbed onto unmodified and modified hulls with associated SAVR (μm^{-1}) for different sized hulls.

Hull Type	Hull Size	SAVR	Copper Q_o	Cadmium Q_o
Unmodified	125-250 μm	0.032	9 ± 2	8 ± 1
	250-500 μm	0.016	5 ± 1	4.7 ± 0.7
	500-1000 μm	0.008	2.5 ± 0.5	4.4 ± 0.4
Modified	125-250 μm	0.032	16 ± 2	17 ± 2
	250-500 μm	0.016	11 ± 4	10 ± 2
	500-1000 μm	0.008	10 ± 1	10 ± 3

The increase in the adsorption capacity for 250-500 μm hulls to 500-1000 μm hulls is not as pronounced, perhaps due to difficulty resolving the increase given the uncertainties in the measurements. Because the true surface area includes a combination of the surface area of the interior pores and the hull's surface, the particle size should not have a significant influence on the adsorption capacity for very porous materials. For instance, the diameter of zeolite particles

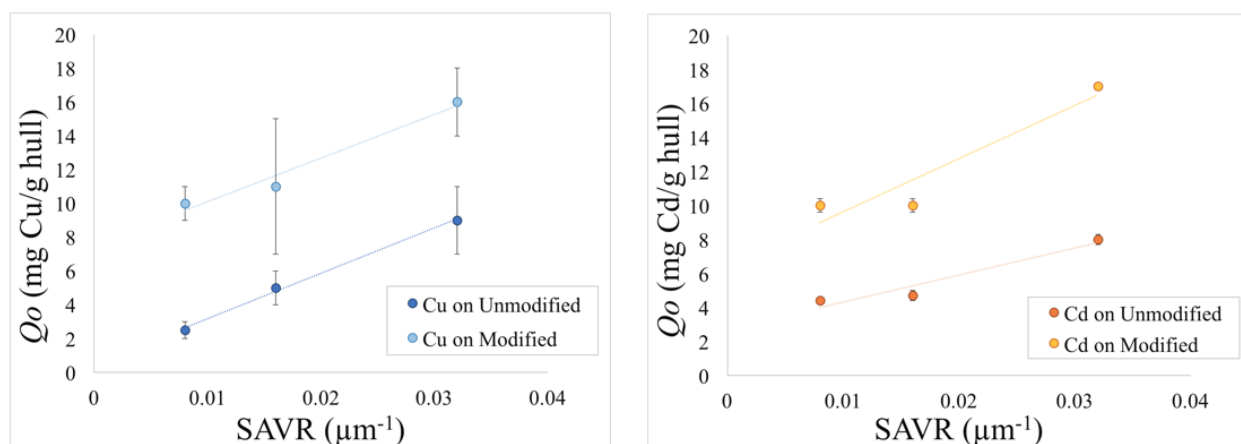


Figure 14. Adsorption capacities Q_o as a function of the surface area to volume ratio (SAVR) for the adsorption of copper and cadmium onto ground peanut hulls in single metal solutions.

does not strongly influence the material's adsorptive capacities because the dominant adsorption process occurs within the particles' pores, rather than on the outer surface of the particle.¹⁶ It is possible that for smaller peanut hull particles, active binding sites within the pores are more accessible and therefore only a slight increase in adsorption capacity is observed as particle size decreases. For larger particles, the pores may be less accessible because they are buried in the interior of the particle, and consequently a decrease in particle size would have a large effect on accessible surface area and therefore adsorption capacity.

Figure 14 shows a comparison of the SAVR for the adsorption of copper and cadmium onto hulls. The linearity shown in the adsorption of copper onto unmodified and modified hulls in single metal studies indicates that binding is predominantly occurring on the surface of the hulls. This correlation is generally the case; however, SAVR neglects to account for the presence of pores where adsorption is also occurring. In cases where the relationship is not linear, interior binding within pores may play a more prominent role.

Figure 13 shows the relative binding strengths, b (ppm^{-1}), of copper and cadmium onto each hull type with their associated uncertainties. For each type of hull and individual metal ion, the relative binding strength is highest for adsorption onto 250-500 μm hulls, which could indicate

that this hull size is ideal for stronger binding of these metal ions.

Effects of Hull Modification. Modified hulls of all sizes have nearly double or more adsorption capacities for both copper and cadmium when compared to the adsorption onto unmodified hulls (see Table 2 and Figure 12). The increase in adsorption capacity is likely due to an increase in porosity in the hulls following the bleaching process, which dissolves lignin from within the hull, creating a higher surface area and more access to additional binding sites on the hull's surface.⁷ The literature shows that an increase in the porosity of high and low density 500-1000 μm hulls was 60% and 150%, respectively.⁷ Because there is more material per individual hull for larger hull sizes, more material (lignin) can be removed during the bleaching process creating a greater change in the surface area of the hull, which results in more exposed binding sites and higher adsorption capacities. Another possible explanation is the oxidation of cellulose hydroxyl groups to carboxylate groups which have a higher affinity to metal cations.^{6,17} This has been shown in the literature for jute fibers⁶ and sugarcane bagasse,¹⁷ but research in this group has not been able to find evidence that this is the case for peanut hulls.⁷

Surface coverage for both copper and cadmium onto modified 250-500 μm and 500-1000 μm hulls in Figures 10 and 11 overlap for concentrations over 200 ppm. This result shows that the 250-500 μm and 500-1000 μm are similar in size and therefore have similar adsorption capacities, which could be due to their larger size being similar enough to have similar porosity changes after modification.

Within the limits of uncertainty, b is about the same for both copper and cadmium for each size of modified hulls. This result, coupled with the similar adsorption capacities seen for each metal onto modified hulls, indicates that copper and cadmium have a similar adsorption behavior for modified hulls.

Effects of Ion Identity. Within the limits of the uncertainty, the adsorption capacities for copper and cadmium are about the same. However, an exception is seen for 500-1000 μm unmodified hulls where the adsorption capacity is higher for cadmium than for copper. This gen-

eral trend is consistent with observations from the literature when these individual metals are adsorbed to tea waste.¹⁸ Literature trends show that the adsorption capacity is higher for copper than for cadmium,^{19–21} however, it has also been reported that cadmium can adsorb more than copper.²² These mixed results indicate that the adsorption of metals is dependent on both the material^{20,23} and the nature of the metal ion.²² The variation in adsorption capacities is due to the different types of interactions that can occur between the sorbent and the sorbate. Binding is a result of ion exchange, the nature of the ion, the material, and size exclusivity. In considering the nature of the ion, copper atoms are smaller in size, meaning a greater number of copper ions could fit onto the hull surface than cadmium ions resulting in a higher Q_o .^{21,24} Additionally, crystal field theory suggests that because copper has a d^9 structure and cadmium has a d^{10} structure, copper has a crystal field stabilization energy (CFSE) while cadmium does not.^{18,25} CFSE could lead to more stable complexes between peanut hulls and copper rather than those formed with cadmium, causing copper to be preferentially adsorbed.^{18,25} However, for both unmodified and modified hulls, copper and cadmium had similar adsorption capacities, so the role of the sorbent may play a more dominant role than ion identity in determining adsorption capacity.^{20,22,23} Another explanation for these results is polarizing power. Polarizing power is the ability of a cation to distort an anion. Cations with smaller ionic radii have higher polarizing power because the positive charge is concentrated in a smaller area. This allows copper, with a smaller ionic radius and higher polarizing power, to have a greater affinity for the negatively or partially negatively charged binding sites on the hulls when compared to cadmium.

For unmodified hulls, the relative binding strength is lower for cadmium than for copper. Therefore, copper binds more strongly to unmodified hulls than cadmium. This result is consistent with copper's higher polarizing power and smaller ionic radius.

Bimetal Mixture Adsorption

For bimetal mixture experiments, the adsorption isotherms are reported for a concentration range of 0–500 ppm to better establish Q_o . With a total metal concentration greater than 1000 ppm, sur-

face coverage becomes increasingly unreproducible and no longer fits the Langmuir equation as discussed previously for single metal adsorption studies. Figures 15 through 20 show q_e vs. C_e data fit to the Langmuir equation (Equation 4) for the adsorption of copper and cadmium onto unmodified and modified hulls. Although surface coverage (q_e) is shown out to 1000 ppm, the Langmuir fit is shown only through 500 ppm to reflect the data that was used to calculate the adsorption capacities and relative binding strengths for binary mixtures. From the fitting parameters, adsorption capacity (Q_o) and relative binding strength (b) were determined and are summarized in Table 4 and Figures 21 and 22, respectively.

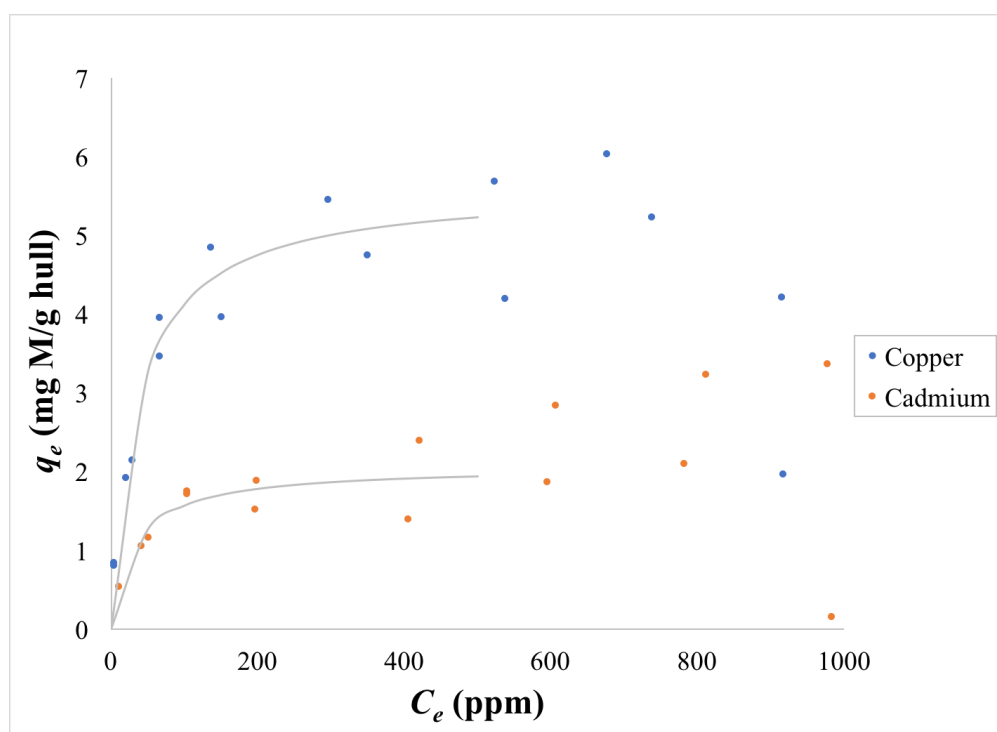


Figure 15. Adsorption isotherms for copper and cadmium adsorbed onto 125-250 μm unmodified hulls in binary metal mixture solutions. The data shown was collected from 2 trials. The solid lines are the fits to the Langmuir equation.

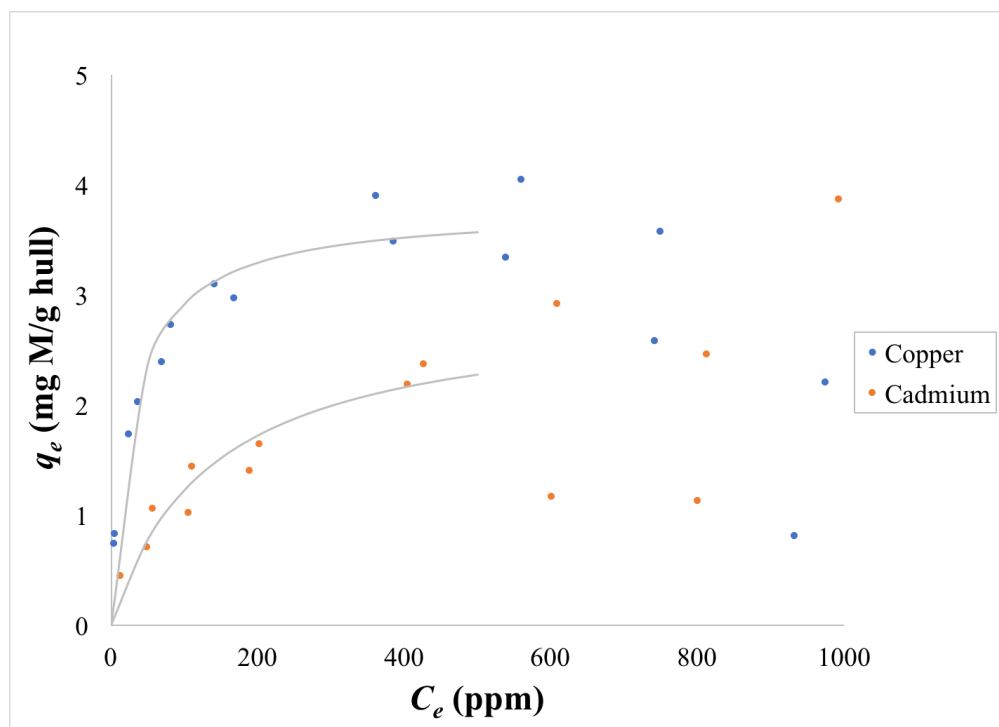


Figure 16. Adsorption isotherms for copper and cadmium adsorbed onto 250-500 μm unmodified hulls in binary metal mixture solutions. The data shown was collected from 2 trials and excludes 1 data point from a concentration above 500 ppm. The solid lines are the fits to the Langmuir equation.

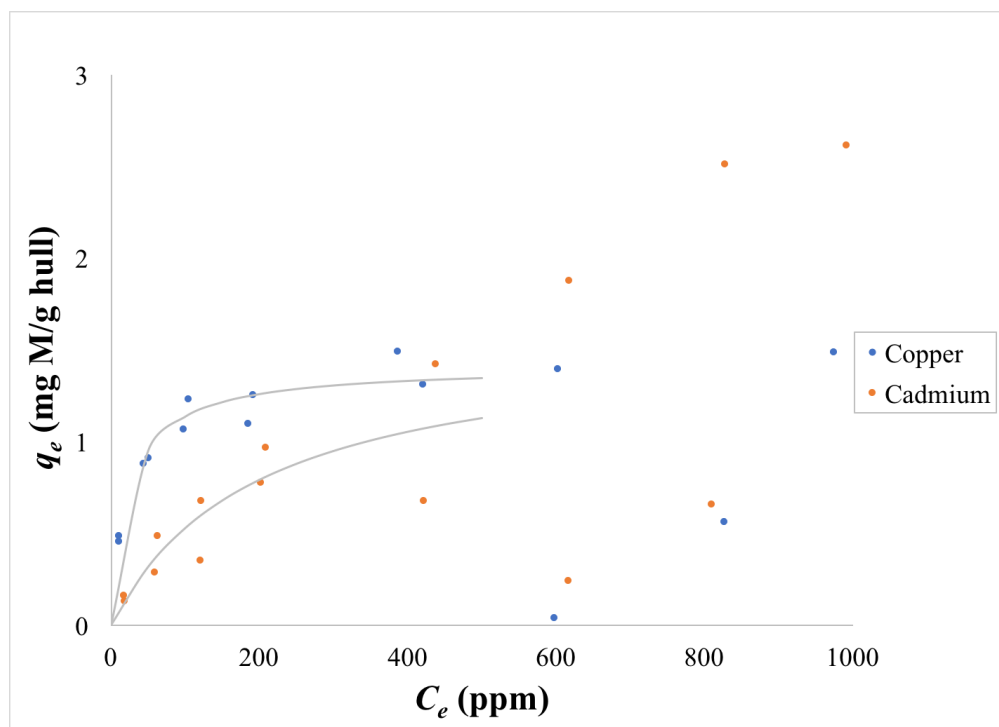


Figure 17. Adsorption isotherms for copper and cadmium adsorbed onto 500-1000 μm unmodified hulls in binary metal mixture solutions. The data shown was collected from 2 trials and excludes 2 data points above the concentration of 500 ppm. The solid lines are the fits to the Langmuir equation.

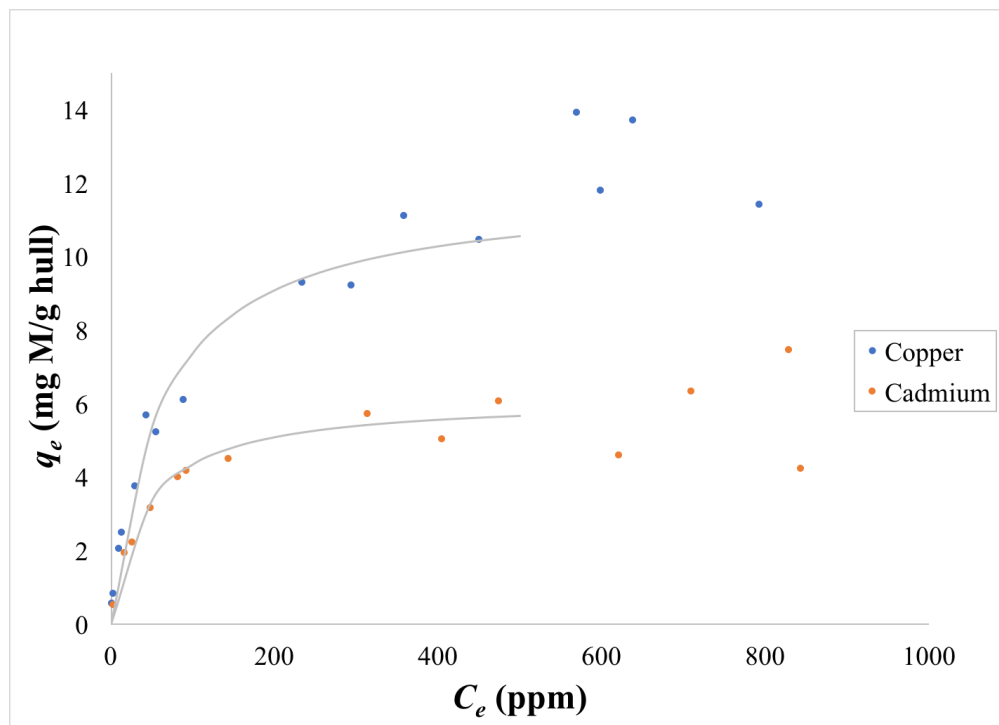


Figure 18. Adsorption isotherms for copper and cadmium adsorbed onto 125-250 μm modified hulls in binary metal mixture solutions. The data shown was collected from 2 trials. The solid lines are the fits to the Langmuir equation.

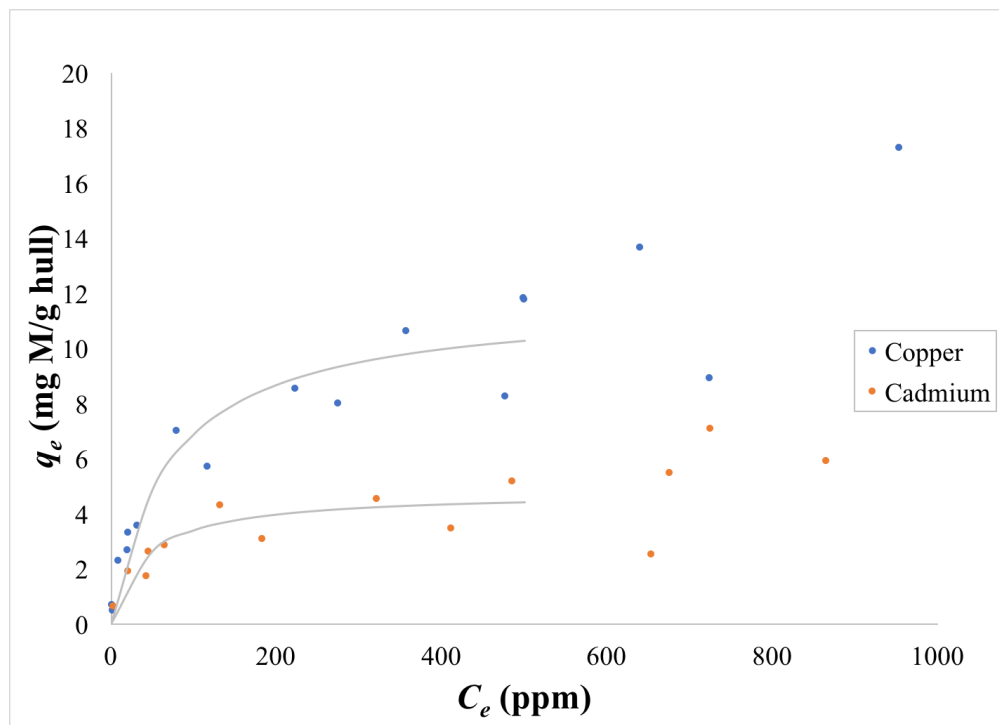


Figure 19. Adsorption isotherms for copper and cadmium adsorbed onto 250-500 μm modified hulls in binary metal mixture solutions. The data shown was collected from 2 trials. The solid lines are the fits to the Langmuir equation.

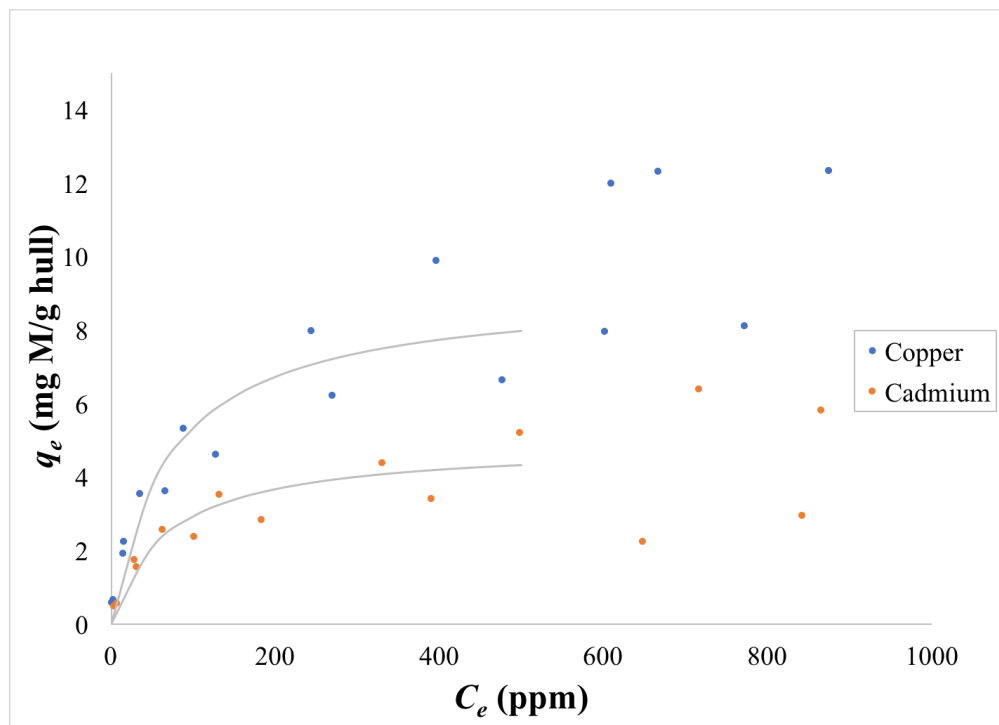


Figure 20. Adsorption isotherms for copper and cadmium adsorbed onto 500-1000 μm modified hulls in binary metal mixture solutions. The data shown was collected from 2 trials. The solid lines are the fits to the Langmuir equation.

Table 4. Binary metal mixture adsorption capacities, Q_o (mg M/g hull), relative binding strengths, b (ppm⁻¹), and associated uncertainties for unmodified and modified hulls.

Hull Type	Hull Size	Copper		Cadmium	
		Q_o	b	Q_o	b
Unmodified	125-250 μm	6 ± 1	0.0277 ± 0.0007	2.1 ± 0.7	0.03 ± 0.01
	250-500 μm	3.8 ± 0.6	0.034 ± 0.007	2.9 ± 0.6	0.007 ± 0.002
	500-1000 μm	1.4 ± 0.2	0.041 ± 0.008	1.6 ± 0.6	0.005 ± 0.003
Modified	125-250 μm	12 ± 1	0.016 ± 0.003	6.1 ± 0.7	0.024 ± 0.003
	250-500 μm	12 ± 3	0.014 ± 0.004	5 ± 1	0.014 ± 0.009
	500-1000 μm	9 ± 3	0.014 ± 0.005	5 ± 1	0.015 ± 0.005

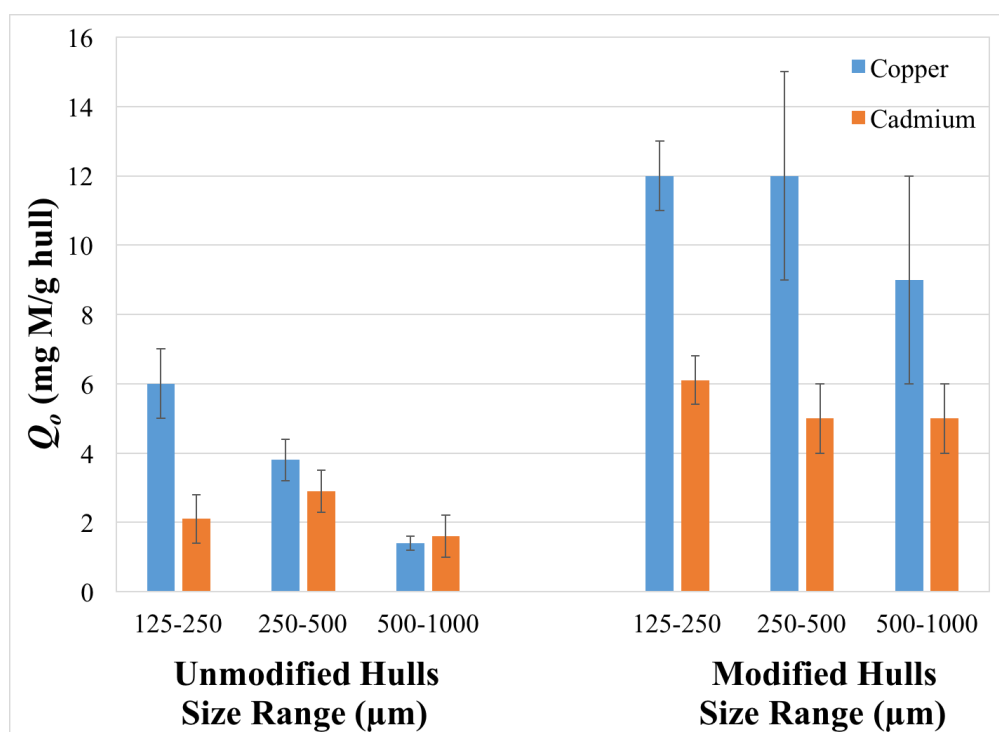


Figure 21. Adsorption capacities, Q_o (mg M/g hull), for copper and cadmium adsorbed onto 125-250 μm , 250-500 μm , and 500-1000 μm unmodified and modified hulls in binary metal adsorption studies with their associated uncertainties, determined from the fit of the adsorption data to the Langmuir equation.

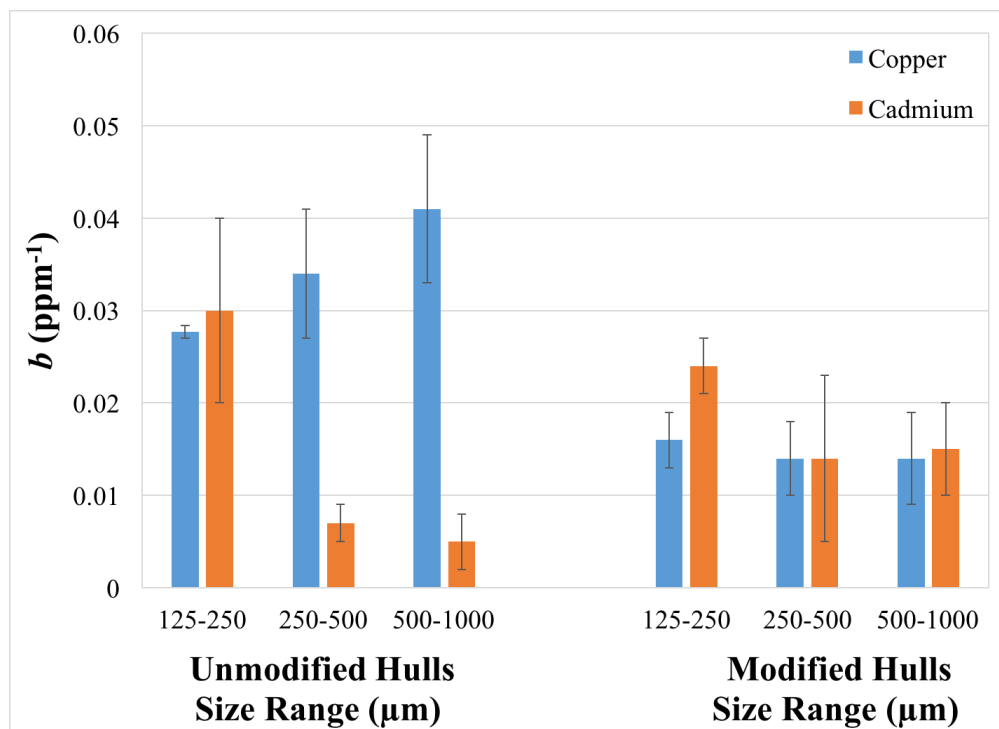


Figure 22. Relative binding strengths, b (ppm⁻¹), for copper and cadmium adsorbed onto 125-250 μm, 250-500 μm, and 500-1000 μm unmodified and modified hulls in binary metal adsorption studies with their associated uncertainties, determined from the fit of the adsorption data to the Langmuir equation.

Effects of Hull Size. Generally, 125-250 μm hulls adsorb the highest amount of both copper and cadmium, while 500-1000 μm hulls adsorb the least. This result shows that the smaller sized hulls have a higher adsorption capacity of both copper and cadmium in binary metal mixtures when compared adsorption using larger hulls, which is similar to what is observed for single metal experiments. As with single metal adsorption, this trend can be explained by the higher surface area to volume ratio (SAVR) and greater pore access of 125-250 μm hulls when compared to those of 500-1000 μm hulls. The correlation between Q_o and SAVR is shown in Table 5 and Figure 23 for binary metal adsorption.

Table 5. Adsorption capacities, Q_o (mg M/g hull), for copper and cadmium adsorbed onto unmodified and modified hulls with associated SAVR (μm^{-1}) for different sized hulls in binary metal mixtures.

Hull Type	Hull Size	SAVR	Copper Q_o	Cadmium Q_o
Unmodified	125-250 μm	0.032	6 ± 1	2.1 ± 0.7
	250-500 μm	0.016	3.8 ± 0.6	2.9 ± 0.6
	500-1000 μm	0.008	1.4 ± 0.2	1.6 ± 0.6
Modified	125-250 μm	0.032	12 ± 1	6.1 ± 0.7
	250-500 μm	0.016	12 ± 3	5 ± 1
	500-1000 μm	0.008	9 ± 3	5 ± 1

The relative binding strengths for copper onto unmodified hulls, shown in Table 4 and Figure 22, increase as hull size increases which could indicate that the larger sized hulls are more ideal for stronger binding of copper in binary metal mixtures. However, the opposite result is observed for the adsorption of cadmium onto unmodified hulls. The highest relative binding strength is for cadmium onto 125-250 μm hulls.

In Figure 25 there is an increase in relative binding strength for the adsorption of cadmium onto unmodified and modified 125-250 μm hulls in binary metal mixtures compared to single metal solutions. However, this trend is not shown for the two larger hull sizes. One possible explanation for the inconsistency in binding strengths is that a bilayer, rather than a monolayer,

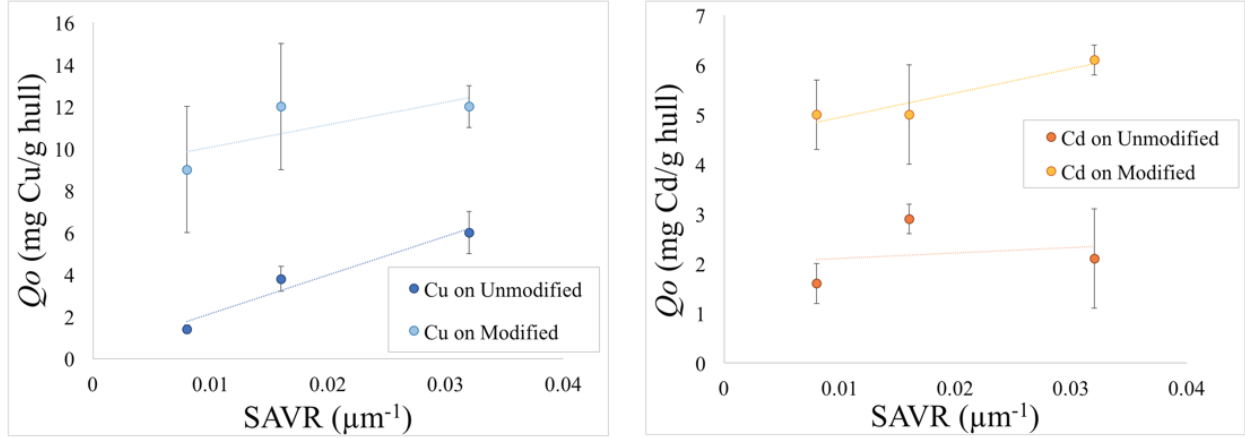


Figure 23. Adsorption capacities (Q_o) as a function of the surface area to volume ratio (SAVR) for the adsorption of copper (left) and cadmium (right) onto ground peanut hulls in binary metal mixtures.

forms during adsorption. In this case, copper's faster v_{rms} allows it to diffuse through solution to occupy binding sites more quickly than cadmium, causing cadmium to bind more often to the hull binding sites from the second layer of metal adsorbed to the hull. Interaction of the first layer with the second layer will affect the strength of the interaction between the first layer and the hull. The interactions are complex due to the presence of counterions and hydration spheres, which likely play a significant role in electrostatic attractive and repulsive forces. The net sum of these interactions would dictate the strength of the interaction of the metals to the hull surface.

Table 6. Relative binding strengths, b (ppm^{-1}), and associated uncertainties for copper and cadmium onto unmodified and modified hulls in single metal solutions and binary metal mixtures.

Hull Type	Hull Size	Copper b		Cadmium b	
		Single	Binary	Single	Binary
Unmodified	125-250 μm	0.011 ± 0.002	0.0277 ± 0.0007	0.009 ± 0.002	0.03 ± 0.01
	250-500 μm	0.020 ± 0.005	0.034 ± 0.007	0.011 ± 0.002	0.007 ± 0.002
	500-1000 μm	0.014 ± 0.004	0.041 ± 0.008	0.0028 ± 0.0004	0.005 ± 0.003
Modified	125-250 μm	0.011 ± 0.002	0.016 ± 0.003	0.009 ± 0.002	0.024 ± 0.003
	250-500 μm	0.021 ± 0.008	0.014 ± 0.004	0.019 ± 0.004	0.014 ± 0.009
	500-1000 μm	0.017 ± 0.003	0.014 ± 0.005	0.017 ± 0.007	0.015 ± 0.005

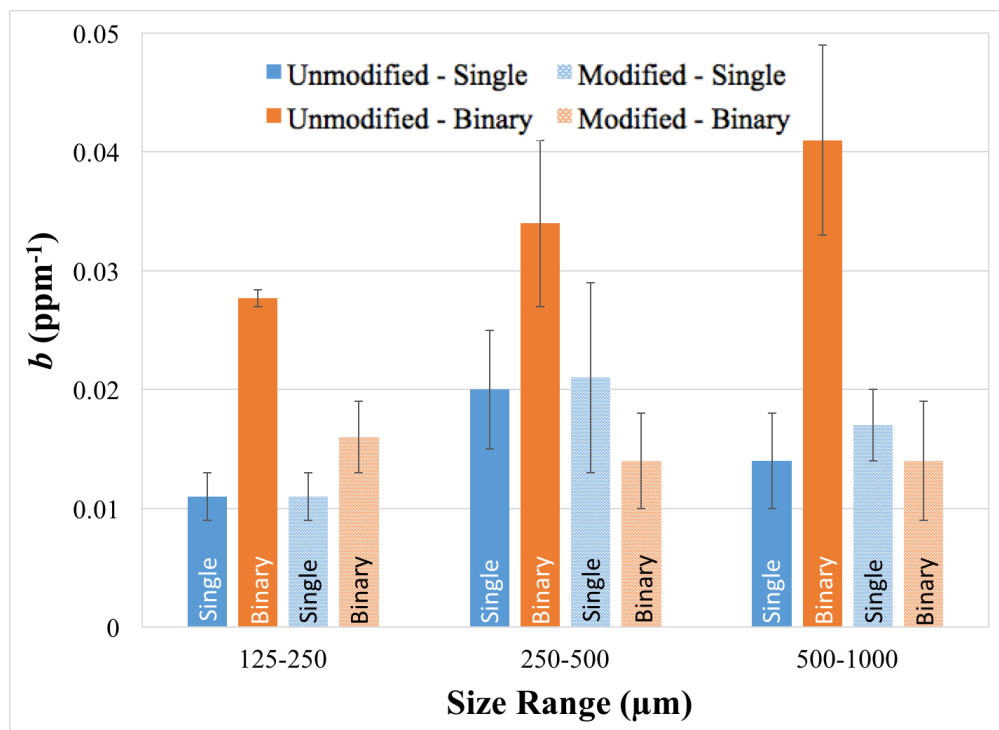


Figure 24. Relative binding strengths, b (ppm^{-1}), for the adsorption of copper onto unmodified and modified hulls in single and binary metal mixtures.

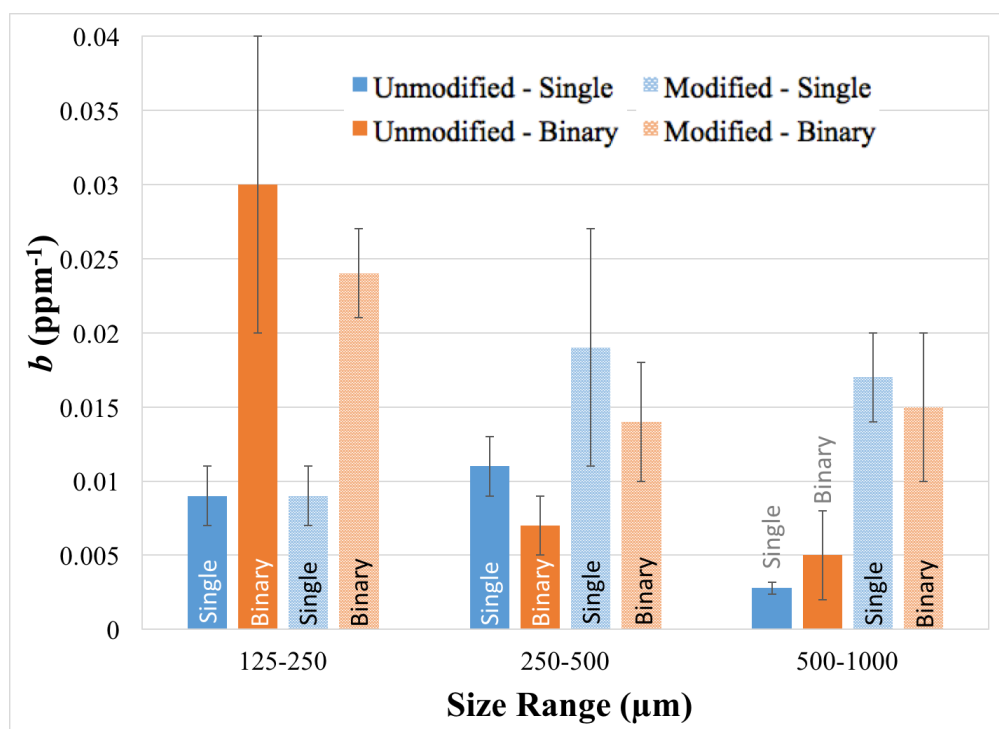


Figure 25. Relative binding strengths, b (ppm^{-1}), for the adsorption of cadmium onto unmodified and modified hulls in single and binary metal mixtures.

Effects of Hull Modification. The adsorption capacities are higher for modified hulls than for unmodified hulls. This behavior is similar to what is observed for single metal adsorption studies and can be explained by the removal of lignin, which increases the number of binding sites.⁷

In binary solutions, the relative binding strength of copper to modified hulls remains constant for all hull sizes. A slight decrease is observed for cadmium. This moderate change suggests that each hull size adsorbs a particular ion with similar binding strength in modified hulls.

The binding strength for each ion to modified hulls in binary solutions is also almost the same as the binding strength in single metal experiments. An exception is seen for the adsorption of cadmium onto 125-250 μm modified hulls, in which b increases relative to the single metal solution. Given that there are not a lot of data points in the low concentration range, the initial slope of the isotherm, which drives the value for b , is not well-defined. Future work should include additional data points in this concentration range before drawing strong conclusions about relative binding strength.

Effects of Ion Identity. Figure 21 shows the adsorption capacities, Q_o (mg M/g hull), of copper and cadmium onto each hull type with their associated uncertainties. In contrast to the results from single metal adsorption, binary metal mixtures show higher adsorption capacities for copper onto unmodified and modified hulls when compared to the adsorption capacities for cadmium. (The only exception is for the adsorption onto unmodified 500-1000 μm hulls, but the uncertainties suggest the capacities for copper and cadmium are approximately the same in this case.) This result is clearly shown by the adsorption capacity ratios in Table 7. The ratios were derived by dividing the copper adsorption capacity (Q_o) by the cadmium adsorption capacity (Q_o) in order to show the preference of the adsorption of copper in the presence of cadmium. Ratios are generally greater than one and all systems show an increase compared to the single metal systems, which means copper adsorption is either favored or increasingly favored over cadmium adsorption in binary metal mixtures. This could be explained by the high polarizing power and small size of copper atoms when compared to cadmium, allowing the copper to have preference of binding sites on the hulls when both are present.^{20,21,24}

Table 7. Adsorption capacities, Q_o (mg M/g hull), and associated uncertainties for copper and cadmium adsorbed onto unmodified and modified hulls. The ratios were derived by dividing the copper adsorption capacity by the cadmium adsorption capacity in order to show the preference of the adsorption of copper in the presence of cadmium.

Hull Type	Hull Size	Single			Binary		
		Q_o Cu	Q_o Cd	Q_o Ratio: (Cu/Cd)	Q_o Cu	Q_o Cd	Q_o Ratio: (Cu/Cd)
Unmodified	125-250 μm	9 ± 2	8 ± 1	1.2 ± 0.3	6 ± 1	2.1 ± 0.7	3 ± 1
	250-500 μm	5 ± 1	4.7 ± 0.7	1.2 ± 0.3	3.8 ± 0.6	2.9 ± 0.6	1.3 ± 0.3
	500-1000 μm	2.5 ± 0.5	4.4 ± 0.4	0.6 ± 0.1	1.4 ± 0.2	1.6 ± 0.6	0.9 ± 0.4
Modified	125-250 μm	16 ± 2	17 ± 2	0.9 ± 0.2	12 ± 1	6.1 ± 0.7	1.9 ± 0.3
	250-500 μm	11 ± 4	10 ± 2	1.1 ± 0.4	12 ± 3	5 ± 1	2 ± 1
	500-1000 μm	10 ± 1	10 ± 3	1.0 ± 0.4	9 ± 3	5 ± 1	1.9 ± 0.7

The crystal field stabilization energy of copper could also be a driving force for increased capacity over that of cadmium. However, since copper adsorption is not favored in single metal solutions, a more likely explanation is a kinetic argument. Using the approximation of the kinetic theory of gases, the root mean square velocity (v_{rms}) is inversely proportional to the atomic mass of the ion (M):

$$v_{rms} = \sqrt{\frac{3RT}{M}} \quad (6)$$

where R is the gas constant and T is the temperature in kelvin.²⁶ If effects due to shaking the solutions, hydration of the ions and inhibition or enhancement of diffusion due to intermolecular interactions are neglected, the v_{rms} for copper and cadmium are proportional to 0.125 and 0.0943 m/s, respectively. A higher v_{rms} means the frequency of collisions with the hull surface would be greater. Essentially, copper ions arrive at the hull surface more quickly than the cadmium ions and are able to attach to binding sites first, resulting in a greater adsorption of copper, a similar Q_o ratio would be observed for binary adsorption. Within the limits of uncertainty, this ratio is correct for four out of the six solutions. However, a thermodynamic driving force may still play a role in the preferential binding of copper.

When compared to the results of the single metal adsorptions, adsorption capacities for copper and cadmium onto each hull type decreased for binary metal mixtures, with the exception of the adsorption of copper to 250-500 μm and 500-1000 μm modified hulls (Table 7). The decrease in the overall adsorption capacities for hulls in binary metal mixtures could be due to the total metal ion concentration within the solution being close to the metal concentrations of 0-1000 ppm used in single metal experiments. A lower adsorption capacity suggests a maximum total ion adsorption capacity exists, regardless of the identity of the ions in the mixture. Research has shown that as the number of metals present in solution increase, Q_o for each metal decreases, while the total metal ion concentration remains constant.²⁷ These results are consistent with the

data, where the combined adsorption capacities for the adsorption of copper and cadmium onto unmodified 125-250 μm hulls in binary metal mixtures is 8.1 μm , while the adsorption capacities are 9 μm and 8 μm for the adsorption of copper and cadmium, respectively, in single metal solutions. A similar trend is seen throughout the binary metal adsorption trials.

The relative binding strengths for the adsorption of both copper and cadmium onto unmodified hulls in binary metal mixtures are shown in Table 6, Figure 24, and Figure 25. With the exception of 125-250 μm unmodified hulls, copper has a higher relative binding strength than cadmium, meaning copper forms a stronger bond to the hull binding sites in the presence of cadmium. For modified hulls, cadmium has a slightly higher b than copper for the 125-250 μm hulls. In the larger hull sizes, b is about the same for copper and cadmium. The complicated results are due to a combination of polarizing power of the ion and its radius, as well as the possibility of mixed metal bilayer formation which can influence binding strength.

CHAPTER FOUR: CONCLUSIONS

Through experimentation it was determined that the factors that influence the adsorption of copper and cadmium onto ground peanut hulls are the nature of the ion, including polarizing power, ionic radius, and v_{rms} , and the material used as the sorbent, including the SAVR. Generally, adsorption capacity increases as particle size decreases in single metal experiments, but in bimetal mixture experiments, the nature of the ion and the material both play a significant role. However, because the surface area includes a combination of the surface area of the interior pores and the hull surface, the particle size does not have a significant influence on the adsorption capacity particularly for smaller hulls in which pores dominate the surface area. Assuming that the porosity of the hulls is uniform among all hull sizes binding is predominantly on the surface of the particle compared to within the pores for large particles because the pores on the larger hulls are less accessible to metals in solution.

The increase in adsorption capacity for modified hulls compared to unmodified hulls in both single metal and binary metal mixture adsorption studies is likely due to an increase in porosity of the hulls following the bleaching process. Another possible explanation is the oxidation of cellulose hydroxyl groups to carboxylate groups which have a higher affinity to metal cations.^{6, 17}

The different combinations of polarizing power and ionic radius of the sorbate and the nature of the sorbent result in a variation of results due to the different types of interactions that can occur.¹⁸ In these studies, copper and cadmium had similar adsorption capacities in single metal adsorption studies. A higher relative binding strength for the adsorption of copper onto unmodified hulls means that copper binds more strongly to unmodified hulls than cadmium.

In contrast, binary metal mixture adsorption studies showed higher adsorption capacities for copper than cadmium. This may be due to copper's higher polarizing power and smaller ionic radius, but also copper's non-zero crystal field stabilization energy. However, the effect may also be due to copper's faster diffusion rate. The relative binding strengths for binary metal mixture ad-

sorption studies were highest for copper onto unmodified hulls, indicating that unmodified hulls bind more strongly to copper than cadmium, again due to copper's higher polarizing power and smaller ionic radius.

CHAPTER FIVE: FUTURE WORK

Future research on this project will examine the adsorption of other metal ions onto ground hulls to determine the universality of adsorption results. These studies will also be used to determine how additional metal ions may compete for access to binding sites. Additionally, it would be highly informative to vary experiment conditions such as temperature, pH, and mixing time to observe how the experimental conditions affect the adsorption of metal ions onto ground peanut hulls and to determine optimum conditions for maximum adsorption. Previous research has shown that higher temperatures and a pH range of 6-10 increased adsorption of heavy metals onto alternative agricultural wastes being investigated for biosorption.⁴

Further research could be conducted using additional hull sizes in order to determine the optimum particle size range. While smaller sized hulls with larger SAVR have higher adsorption capacities for copper and cadmium, research has shown there are adverse affects to using particles that are too small.²⁸ A pelletizing method that uses fine particles bound together by a porous binding agent, similar to that use by Johnson et al.,³ could be developed.

While batch studies inform researchers about equilibrium adsorption behavior, they do not closely model the behavior of continuous flow systems used for industrial remediation processes. Column studies have been performed for copper onto peanut hulls,¹³ but could be further investigated for cadmium and metal mixtures. Additionally, conducting kinetics studies on the adsorption of copper and cadmium in binary metal mixtures could shed light on the competition between these metals for hull binding sites. Higher resolution measurements at the lowest concentrations may better establish a more accurate value for relative binding strength.

Lastly, a cost comparison of using ground peanut hulls vs. other commercial sorbents can be performed. Though molecular modification of hulls raises operational costs through the use of additional reagents, increased adsorptivity and low initial investment in agricultural wastes may sufficiently compensate for this cost and create an overall more cost effective alternative to

current adsorption methods.⁴ Spent biosorbents also have the potential to be regenerated and the metals reclaimed, reducing the overall waste generated from this type of heavy metal remediation technique significantly.⁴

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